

by Jesús Martínez-Frías

# An ancient Ba-Sb-Ag-Fe-Hg-bearing hydrothermal system in SE Spain

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*A significant characteristic of the Neogene-Quaternary volcanic province of SE Spain is its spatial and temporal relationship with gold, silver, Fe-Mn, Hg-Sb, and base-metal sulphide hydrothermal mineralization. All these deposits comprise a metallogenetic belt, which extends from the Cabo de Gata Natural Park (Almería province) to Cartagena (Murcia province). With the exception of the famous gold-rich volcanic area of Rodalquilar, the hydrothermal systems of SE Spain are represented by the mineral deposits rich in Ba-Sb-Ag-Fe-Hg at Las Herrerías and Valle del Azogue. The principal characteristics of these two areas are the following: 1) presence of the most important deposit of shallow marine, sulphide bearing exhalites of Spain; 2) existence of the largest fossil fumaroles in Europe related with the mineralization process, and 3) occurrence of cinnabar in relation with the Sb-rich veins. The study of these two mineralized areas has made it possible to define, for the first time, an ancient Ba-Sb-Ag-Fe-Hg bearing hydrothermal system.*

## Introduction

The Neogene volcanic province of SE Spain is located to the east of the Betic Cordillera and extends from Cabo de Gata (Almería) to Cartagena (Murcia) (Mediterranean margin). The magmas generated in this region include the following rock series: calc-alkaline, K-rich calc-alkaline, shoshonitic, ultra-potassic and alkaline basaltic. Radiometric dating indicates that there were two episodes of magmatic activity. The first of these episodes began in the Late Burdigalian/Early Langhian with the generation of the calc-alkaline rocks, continued with the simultaneous extrusion of the calc-alkaline, K-rich calc-alkaline and shoshonitic rocks, and ended in the Messinian with the emplacement of the ultrapotassic rocks. The second episode began 2 Ma later, with the generation of the alkaline basalts (López Ruiz and Rodríguez Badiola, 1980; Nobel et al., 1981; Bellon et al., 1983; Di Battistini et al., 1987).

A significant characteristic of this volcanic province is its spatial and temporal relationship with gold, silver, Fe-Mn, Hg-Sb, and base-metal sulphide hydrothermal mineralization. These deposits comprise a metallogenetic belt, which also extends from Cabo de Gata to Cartagena. Mineralization is hosted in many types of Formations (e.g. Rodalquilar, Mazarrón: volcanic Formations; Las Herrerías: sedimentary Formations; Sierra Almagrera and Sierra Almería: metamorphic Fms., etc.), which form part of the southeastern quarter of the Iberian Peninsula (eastern Betic Cordillera and Iberian foreland). From a geotectonic point of view, the whole structuration of this Cordillera has been regarded in terms of compressional nappe

tectonics and subduction/collision scenarios ranging in age from late Cretaceous to middle and even late Miocene. The gravitational collapse of this orogenic edifice through low-angle extensional detachments, associated to crustal upward arching, isostatic rebound, exhumation of metamorphic and mantle core complexes and volcanism, during middle to upper Miocene times, has also been proposed (Doblas et al., 1991).

Different references about the characteristics of the mineralizing fluids, paragenetic sequences, fluid inclusions, stable isotopes and many other aspects concerning these deposits can be found in Arribas et al. (1989), Martínez-Frías et al. (1989), Martínez-Frías (1991), Manteca and Ovejero (1992), Rodríguez (1993), Martínez-Frías (1993), Morales (1994), Arribas et al. (1995), Martínez-Frías (1997), Serna (1997), Martínez-Frías et al. (1997). Nevertheless, the source of these metals is still a point of some controversy. They either come from the actual regional volcanic complex or they are extracted from the metamorphic formations which were affected by the volcanism.

With the exception of the Rodalquilar caldera, the hydrothermal systems of SE Spain are represented by mineral deposits rich in Ba-Sb-Ag-Fe-Hg of Las Herrerías and Valle del Azogue (Almería province). The principal characteristics of these two areas are the following: 1) presence of the most important deposit of shallow marine, sulphide bearing exhalites of Spain; 2) existence of fossil fumaroles related with the mineralization process, with the largest structures in Europe; 3) occurrence of cinnabar in relation with the Sb-rich veins.

## Las Herrerías

The stratabound-type mineral deposit of Las Herrerías is an excellent example of Upper Miocene, sea-floor, hydrothermal mineralization in SE Spain (Neogene Vera-Garrucha basin) (Figure 1). The ore bodies (mainly barite, jasper, Fe-(±Mn) oxides and hydroxides



**Figure 1** View of the central zone of Las Herrerías sedimentary basin, showing one of the abandoned mine dumps.

—crusts and pipes—, and native silver), are capped by the largest deposit of exhalites in Spain (more than 200 m in lateral extension and a thickness of around 10 m). ICP-MS analyses from pipes and crusts indicate significant contents in Fe (20.20–42.20%), Mn (521–45230 ppm), Ba (110–40180 ppm), Pb (88–1996 ppm), Sb (10–1433 ppm), Zn (98–4571 ppm) and Ag (2.9–175 ppm). The exhalites are made up of mm- to m-sized alternating horizontal beds of barite and red jasper. Tiny inclusions of KCl, Ti-bearing hematite and sulphides (pyrite, sphalerite, galena and cinnabar) are found disseminated within the jasper. High amounts of  $\text{Fe}_2\text{O}_3$  (21.36 wt%), Pb (2243 ppm), Sb (1200 ppm), Zn (404 ppm), As (180 ppm) and Ag (142 ppm) were detected above all in the jasper-rich beds. Both barite- and jasper-bearing exhalites exhibit almost identical rare earth distribution patterns, with LREE > HREE and a very pronounced positive anomaly of Eu (up to 69 ppm). As previously defined, this area includes the most important outcrop of fossil fumaroles in Europe. Three types of fumaroles have been observed (Martínez-Frías et al. 1992): 1) “pores” of millimetric size dispersed throughout the marls affected by the fumarolic activity; 2) small cross-fractures, of N-S and N20–25W strike, with maximum width and length of 10 cm and 2 m respectively; and 3) small tubes and concentric circular structures (up to 6 rings), whose diameters vary from 5 to 50 cm. These structures preserve even the central orifice, which served as the conduit for the hydrothermal fluids. Sometimes, they stand out above the marls some 10 cm, opening upwards in the form of a “mushroom”. Among this last type of fumarole, two textural subtypes can be distinguished: a) bodies with partial recrystallisation and alternating hard and soft concentric bands (abundant), and b) totally recrystallised bodies (scarce), in which the marls suffered a total mineralogical and textural transformation and a strong silica cementing.

Paleobathymetry data offered by Montenat & Seilacher (1978) for the time of emplacement of the hydrothermal fluids (Upper Tortonian–Upper Messinian) indicate an approximated depth of 200–300 m beneath the sea. It has been proposed that the shallow-marine depositional model for the mineralizing fluids could be similar to the Strens and Cann (1982) model of “convection through crack zones”. Thus, Las Herrerías deposit could be defined, in accordance with the Bonnatti (1983) classification, as a syn-postdepositional, undersea, hydrothermal mineralization, in which metals (mainly Fe, Mn, Ag, Pb and Zn) together with other associated elements (mainly Ba, Ca, Si) would form part of very concentrated

solutions, because mineral deposition produced close by the hydrothermal vents.

## Valle del Azogue

The Valle del Azogue (VA) is located within a small trough in the NE margin of the Sierra Almagrera (Betic Cordillera, SE Spain) (Figure 3). Specifically, the main mineralized outcrop is found where the Sierra Almagrera Permian-Triassic metamorphic basement and Neogene marls, sandy marls and limestones meet. The mineralization host rocks are graphitic phyllites, quartz phyllites and metavolcanites. Three tectonic systems have been found in the VA area: N-S faults, which apparently control the positioning of the min-



**Figure 3** Old mine works in the Valle del Azogue area.

eralization, and less developed NE-SW and E-W faults. The entire area is tectonically active (the nearby village of Vera was destroyed by an earthquake in 1518 A.D.).

On the surface, the VA mineral deposit consists of a hydrothermal breccia stretching approximately 1 km N-S, NE-SW and 500 m E-W, which is a striking white (due to the presence of kaolinite) and therefore easily recognizable in the field. The kaolinite, together with quartz, barite, calcite, sericite, gypsum and minor base-metal sulphides (sphalerite, pyrite), are the main components of the breccia.

Combined ICP-AES and ICP-MS analyses of the breccia indicate significant anomalies of Fe, Mn, Ba, Hg, Sb, Zn, Ag, As and Pb which can reach: Fe ( $\text{Fe}_2\text{O}_3 > 6$  wt%), Mn (> 600 ppm), Ba (> 4000 ppm), Hg (> 3000 ppm), Sb (> 10000 ppm), Zn (> 2000 ppm), Ag (> 100 ppm), As (> 800 ppm) and Pb (> 1200 ppm). The morphology of the mineralization changes at depth to a stockwork which reaches at least 100 m beneath the surface (this is the bottom level of the old mine shafts). This stockwork cuts through the Permian-Triassic metamorphic host rocks and branches out at the top of the deposit giving rise to a dense network of small veins. Where the gangue is richest in quartz there is a higher proportion of sulphides. The stock-



**Figure 2** Cylindrical fumarole structure which forms part of the mineralizing venting system. The shallow-marine hydrothermal chimney, unique in Europe, is located east of Las Herrerías' open pit. The different rings visible in the photo do not imply differences in composition (silicified sandy marls), with the exception of the very central part close to the orifice, which is rich in iron.

work mineralization consists of a simple paragenesis which comprises (in order of abundance) quartz, barite, stibnite, cinnabar, sphalerite, siderite, chalcoppyrite and pyrite. Vein-related hydrothermal alteration is poorly developed and it is only represented by the presence of silica followed by sericite. Microprobe analyses of stibnite, sphalerite and pyrite indicate that they display very pure compositions. Nevertheless, small amounts of As in stibnite (As: 0.11–0.29% wt%) and in pyrite (As: 0.20–0.50% wt%), and Fe (2.33–2.80% wt%) in sphalerite were detected.

## Mineralizing hydrothermal solutions

Concerning the nature of the mineralizing solutions for the Herreñas-Azogue mineralizing hydrothermal system, three types of fluid inclusions have been found (López-Gutiérrez et al., 1994): 1) two-phase (L+V) inclusions, with CO<sub>2</sub>, in which the vapor phase occupies 50–70% of the total volume (TH = 330–360 °C); 2) aque-

ous, two-phase (L+V) inclusions, without CO<sub>2</sub>, in which the vapor phase occupies 25–40% of the total volume [with the additional presence of trapped solids (KCl and haematite) (TH = 270–350 °C)], and 3) aqueous, two-phase (L+V) or three-phase (S+L+V) inclusions (TH = 160–260 °C). In broad terms, an increase of salinity linked to a loss of vapor is the general tendency in relation with the descent of temperature. Isotopic values of  $\delta^{34}\text{S}$  in barites range between 23.3 and +23.6 ‰ (Martínez-Frías et al., 1989). However, Morales (1994), referring to the Sierra Almagrera mineralized area (vein type mineralization which is close to Las Herreñas), indicates lower temperatures (145–258 °C), salinities ranging from 3 to 7 wt% eq. NaCl which are not affected by the cooling of the solutions, and a more significant variation (between +18.2 and +23.4 ‰) of  $\delta^{34}\text{S}$  in barites.

The whole mineralizing hydrothermal system has been defined as convective (Navarro et al., 1992) and genetically related to the latest stages of Upper Miocene shoshonitic-type calc-alkaline volcanism (Figure 4), the outcrops of which are located at SW from the VA area, in the Alifraga area (Vera-Garrucha basin).

## Conclusion

The geologic and metallogenetic studies that were carried out in SE Spain display, for the first time, the existence of an ancient Ba-Sb-Ag-Fe-Hg- bearing hydrothermal system. The principal mineralized outcrops are well represented in the Las Herreñas and Valle del Azogue areas (Almería province). In the Las Herreñas area, the ore bodies (mainly barite, jasper, Fe-(±Mn) oxides and hydroxides — crusts and pipes —, and native silver), are capped by the largest deposit of exhalites in Spain (more than 200 m in lateral extension and a thickness of around 10 m). The exhalites are made up of mm- to m-sized alternating horizontal beds of barite and red jasper. Tiny inclusions of KCl, Ti-bearing hematite and sulphides (pyrite, sphalerite, galena and cinnabar) are found disseminated within the jasper. In the Valle del Azogue area, kaolinite, together with quartz, barite, calcite, sericite, gypsum and minor base-metal sulphides (sphalerite, pyrite), are the main components of the hydrothermal breccia.

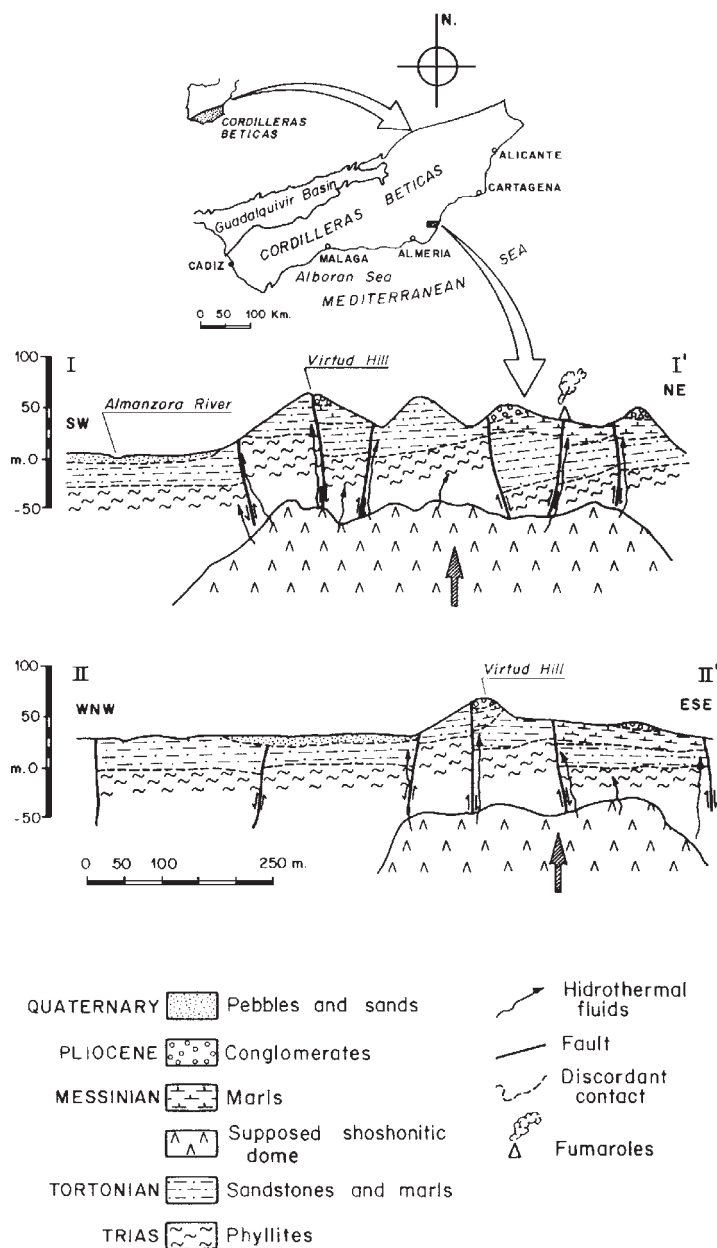
The whole mineralizing hydrothermal system has been defined as convective, displaying a range of temperature between 160 °C and 360 °C, in probable connection with the latest stages of Upper Miocene shoshonitic-type, calc-alkaline volcanism.

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**Figure 4** Idealized geologic sketch displaying how the mineralizing hydrothermal fluids affected the study area during Upper Miocene times. Note the supposed shoshonitic dome.

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